

## PLASMA PROCESSING METHOD

### Field of the Invention

5           The present invention relates to a plasma processing method.

### Background of the Invention

10           Recently, along with the trend for high density and high integration of semiconductor devices, there has been increased demand for forming holes (or grooves) having a high aspect ratio. Moreover, it is preferable that such a hole has a smooth sidewall approximately perpendicular to a  
15           surface of an opening thereof.

          A plasma etching is conventionally used in forming holes having a high aspect ratio in a silicon layer, by adopting certain etching conditions exemplified below.

          Conventionally, a plasma etching process is carried  
20           out by setting the temperature of a lower electrode on which an object to be processed is mounted in a hermetically sealed processing chamber to be not greater than, e.g., 60 °C, and the inner pressure thereof to be lower than or equal to 150 mTorr, wherein a gaseous mixture of HBr, NF<sub>3</sub>  
25           and O<sub>2</sub> gases or HBr, SF<sub>6</sub> and O<sub>2</sub> gases is used as a processing gas.

US Patent No. 5,423,941 also discloses a method for performing an etching by using a gaseous mixture of HBr gas, SiF<sub>4</sub> gas, SF<sub>6</sub> gas, and O<sub>2</sub> gas containing He gas as a processing gas in an airtightly sealed processing chamber, wherein the pressure in the processing chamber is set to be between 50 and 150 mTorr and a magnetic field of a magnitude smaller than or equal to 100 Gauss is applied perpendicular to an electric field.

In the above etching methods, since HBr gas and/or SiF<sub>4</sub> gas is included in the processing gas, a protective layer is formed on an inner sidewall of a hole. Accordingly, it is possible to vertically form a hole having an opening diameter smaller than or equal to 1 μm according to the size of a mask.

In the aforementioned conventional methods, however, deposits (e.g., SiBr<sub>x</sub>O<sub>y</sub>, x and y being the combination ratios) may be accumulated at the openings of the mask. If an opening diameter of the mask is large, such deposits do not affect the etching process. However, when an opening diameter of the mask becomes smaller than or equal to about 0.2 μm, the deposits accumulated at the openings of the mask may present a hampering effect on a fine patterning of the hole.

In case the deposits are accumulated at the opening of the mask, the opening diameter becomes narrower and, consequently, an apparent aspect ratio of the hole increases.

An increase in the aspect ratio results in a decrement of an etching rate and, further, a deterioration in the throughput. In addition, if the aspect ratio is greater than or equal to, e.g., 50, it becomes difficult to etch a bottom portion of the hole, so that the hole may not attain a designed depth.

#### Summary of the Invention

It is, therefore, a primary object of the present invention to provide a new and improved plasma processing method capable of forming fine holes (or grooves) of a high aspect ratio in a silicon layer with a high etching rate.

In accordance with the present invention, there is provided a plasma processing method including the step of: etching a silicon layer of an object to be processed by employing a patterned mask and by using a plasma of a processing gas introduced into an airtight processing chamber, the processing gas containing a gaseous mixture in which one or both of  $\text{SF}_6$  gas and  $\text{NF}_3$  gas are added to  $\text{HBr}$  gas,  $\text{O}_2$  gas and  $\text{SiF}_4$  gas, wherein a gas containing C and F is further added to the processing gas. Due to an effect of the gas containing C and F, deposits are prevented from being accumulated at an opening of the mask and, further, accumulated deposits are removed. Accordingly, it is possible to form a deep hole in a silicon layer even in case a diameter of a opening of the mask is very small.

The gas containing C and F may be a gaseous mixture having a combination of one or more gases selected from the group consisting of  $\text{CF}_4$  gas,  $\text{C}_4\text{F}_8$  gas,  $\text{C}_5\text{F}_8$  gas,  $\text{C}_4\text{F}_6$  gas,  $\text{CHF}_3$  gas and  $\text{CH}_2\text{F}_2$  gas.

5           In order to prevent deposits from being accumulated at the opening of the mask or remove accumulated deposits, it is preferable to set the flow rate of the gas containing C and F added to the processing gas to be smaller than or equal to, e.g., 10 sccm. Further, the added amount of the  
10           gas containing C and F is preferably controlled according to the material or thickness of the mask or the etched amount of the silicon layer. Furthermore, the patterned mask preferably includes at least an oxide layer containing silicon.

15           In accordance with the present invention, the addition of the gas containing C and F to the processing gas may be initiated either from the beginning or at a certain stage of the etching process of the silicon layer of the object to be processed and then terminated before or continued until the  
20           end of the etching process. The time period of supplying the gas containing C and F is preferably set based on, e.g., the accumulating state of deposits at the opening of the mask and an opening diameter of a hole or an opening width of a groove formed by the etching. Accordingly, deposits are  
25           prevented from being accumulated at the opening of the mask. Further, even if the deposits are excessively accumulated

thereat, it is possible to appropriately remove the deposits.

Especially, in case the opening diameter of the hole or the opening width of the groove formed by the etching is smaller than or equal to about 0.2  $\mu\text{m}$ , the accumulation of deposits at the opening thereof has been problematic. Since, however, the accumulation of deposits at the opening of the mask is suppressed in accordance with the present invention, it is possible to form deep holes or deep grooves in a silicon layer even in case the opening diameter of the holes or the opening width of the grooves is smaller than or equal to about 0.2  $\mu\text{m}$ .

Further, as used in this specification, 1 mTorr and 1 sccm correspond to  $(1 \times 10^{-3} \times 101325/760)$  Pa and  $(1 \times 10^{-6}/60)$   $\text{m}^3/\text{sec}$ , respectively.

#### Brief Description of the Drawings

The above and other objects and features of the present invention will become apparent from the following description of preferred embodiments, given in conjunction with the accompanying drawings, in which:

Fig. 1 shows a schematic cross sectional view illustrating a plasma processing apparatus in accordance with a preferred embodiment of the present invention;

Fig. 2 describes a schematic cross sectional view of an object to be processed before a mask for use in etching a

silicon layer is formed;

Fig. 3 provides a schematic cross sectional view of the object to be processed after the mask for use in etching the silicon layer is formed;

5 Figs. 4A to 4C represent schematic cross sectional views of the object to be processed, showing accumulating states of deposits at openings of the mask;

Figs. 5A to 5C offer schematic cross sectional views of the object to be processed, showing states of holes  
10 formed on a silicon layer; and

Fig. 6 presents a graph indicating a relationship between an opening diameter of the mask and an etching time.

#### Detailed Description of the Preferred Embodiment

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A preferred embodiment of the plasma processing method in accordance with the present invention will now be described in detail with reference to the accompanying drawings. In the specification and the accompanying drawings,  
20 like reference numerals will be given to like parts having substantially the same functions, and redundant description thereof will be omitted.

Fig. 1 is a schematic cross sectional view showing the structure of a plasma processing apparatus 100 in accordance  
25 with a preferred embodiment of the present invention. A processing chamber 102 of the plasma processing apparatus

100 is made of, e.g., aluminum having an alumite processed (anodizing processed) surface covered by a plate member (not shown) made of quartz. Further, the processing chamber 102 is grounded as illustrated in Fig. 1.

5        Disposed inside the processing chamber 102 is a lower electrode 104 also serving as a susceptor for mounting thereon an object to be processed, e.g., a semiconductor wafer W. The lower electrode 104 can be vertically moved by an elevating shaft (not shown).

10        Formed under a bottom surface of the lower electrode 104 are a quartz member 105 to be an insulating material and a conductive member 107 being in contact with a bellows 109. The bellows 109 made of, e.g., stainless steel, is in contact with the processing chamber 102. Accordingly, the  
15        conductive member 107 is grounded via the bellows 109 and the processing chamber 102. Further, a bellows cover 111 is installed in such a way that it surrounds the quartz member 105, the conductive member 107 and the bellows 109.

20        An electrostatic chuck 110 connected with a high voltage DC power supply 108 is installed to a mounting surface of the lower electrode 104 on which the object to be processed is mounted. Further, a focus ring 112 is provided around the electrostatic chuck 110.

25        Connected with the lower electrode 104 via a matching unit 116 is a dual system of a high frequency power supply, i.e., a first high frequency power supply 118 and a second

high frequency power supply 138. The frequency of a power  
outputted from the first high frequency power supply 118  
(hereinafter, referred to as a first frequency) is set to be  
higher than that from the second high frequency power supply  
5 138 (hereinafter, referred to as a second frequency).  
Accordingly, in the plasma processing apparatus 100, dual  
high frequency power is applied to the lower electrode 104  
and each frequency power is controlled independently.  
Consequently, it is possible to avoid a phenomenon in which  
10 sidewalls of the holes formed on the object to be processed  
are eroded into a curved shape, i.e., the so-called bowing  
phenomenon, thereby providing holes having comparatively  
appropriate shapes.

It is preferable to set the first frequency to be  
15 greater than or equal to, e.g., 27.12 MHz. Especially, in  
case a magnetic field is not generated in a processing space,  
it is preferable to set the first frequency to be greater  
than or equal to 27.12 MHz. On the other hand, in case a  
magnet 130 and the like are provided to generate a magnetic  
20 field in the processing space, the first frequency can be  
set at 13.56 MHz, as will be further described later. This  
is because the density of a plasma can be increased to  
augment an etching rate of silicon by the magnetic field.  
In this case, the second frequency is preferably set at,  
25 e.g., 3.2 MHz.

Provided at a top portion of the processing chamber



102 is an upper electrode 124 grounded therethrough. Further, formed at the upper electrode 124 is a plurality of gas inlet holes 126 for introducing a processing gas. Each of the gas inlet holes 126 is connected with a gas supply source (not shown), and the processing gas is introduced into a processing space 122 via the gas inlet holes 126.

Provided outside the processing chamber 102 is a magnet 130 for generating a horizontal magnetic field to the processing space 122. Due to the magnet 130, a magnetic field of a magnitude of 170 Gauss is generated at a central portion of the object to be processed in the processing space 122. In case the magnitude of the magnetic field generated by the magnet 130 is greater than or equal to 170 Gauss, a high frequency power supply may be configured to provide a single high frequency of, e.g., 13.56 MHz.

Installed at a lower portion of the processing chamber 102 is an exhaust opening 128 connected with an exhaust system (not shown) such as a vacuum pump and the like. Due to such configuration, an inner space of the processing container 102 can be maintained at a certain vacuum level.

Hereinafter, operation of the plasma processing apparatus 100 will be described with reference to Figs. 1 and 2. Fig. 2 shows a schematic cross sectional view of an object to be processed 200 before being etched.

As the object to be processed 200, a semiconductor wafer W having a diameter of, e.g., 200 mm, is used. As

shown in Fig. 2, formed on a surface of the semiconductor wafer W is a resist layer 202 on which holes having a diameter of 150 nm are patterned by a photolithography process. Further, a silicon dioxide film layer ( $\text{SiO}_2$  film) 204, e.g., a CVD oxide film, having a thickness ranging from about 700 to 2200 nm is formed beneath the resist layer 202. Furthermore, a silicon nitride film layer ( $\text{SiN}$  film) 206 having a thickness of about 200 nm is formed beneath the silicon dioxide film layer 204. In some cases, a silicon dioxide film layer ( $\text{SiO}_2$  film) having a thickness smaller than or equal to a few nm may be formed as a gate insulating film between the silicon nitride film layer 206 and a silicon (Si) layer 210.

An etching process is performed on the above-described object to be processed 200 by using the resist layer 202 as a mask, to thereby provide patterning of the silicon dioxide film layer 204 and the silicon nitride film layer 206. Thereafter, the resist layer 202 is removed, as illustrated in Fig. 3. The silicon dioxide film layer 204 and the silicon nitride film layer 206 serve as a mask for etching the silicon layer 210.

Next, the object to be processed 300 having as the mask the silicon dioxide film layer 204 and the silicon nitride film layer 206 that are patterned in a predetermined shape is loaded into the processing chamber 102 via a loading/unloading opening (not shown) and then mounted on

the lower electrode 104. After the processing chamber 102 is evacuated through the exhaust opening 128 by using the vacuum pump (not shown), a processing gas is introduced from the gas supply source (not shown) into the processing chamber 102 via the gas inlet holes 126.

As for the processing gas, a gaseous mixture in which  $\text{CF}_4$  gas is added to  $\text{HBr}$  gas,  $\text{NF}_3$  gas,  $\text{SiF}_4$  gas and  $\text{O}_2$  gas is used. Further, it is possible to use  $\text{SF}_6$  gas instead of  $\text{NF}_3$  gas. The flow rate of each gas in the processing gas is controlled as follows:  $\text{HBr}$  gas ranging from 100 to 600 sccm;  $\text{O}_2$  gas, from 1 to 60 sccm;  $\text{SiF}_4$  gas, from 2 to 50 sccm;  $\text{SF}_6$  gas, from 1 to 60 sccm;  $\text{NF}_3$  gas, from 2 to 80 sccm; and  $\text{CF}_4$  gas, from 5 to 50 sccm.

By controlling the flow rate of the processing gas at a predetermined value, the pressure in the processing chamber 102 can be set under a predetermined level, e.g., 200 mTorr, while setting the temperature of each unit at a predetermined temperature. Moreover, the first high frequency power having the first frequency is applied from the first high frequency power supply 118 to the lower electrode 104 via the matching unit 116 and, at the same time, the second high frequency power having the second high frequency is applied from the second frequency power supply 138 thereto via the matching unit 116.

As described above, the first frequency is preferably chosen to be greater than or equal to 27.12 MHz. Therefore,

the first frequency involved herein is set to be 40.0 MHz. In the meantime, the second frequency is set to be 3.2 MHz. In addition, the output power of the first high frequency power supply 118 is controlled at a value ranging, e.g.,  
5 from 400 to 600 W, and that of the second high frequency power supply 138 is controlled at a value ranging, e.g., from 100 to 800 W.

By supplying the high frequency powers having different frequencies of the dual system to the lower  
10 electrode 104, the dissociation of the processing gas is facilitated and, therefore, the silicon layer 210 can be etched more efficiently.

When the plasma processing apparatus 100 is ready as described above, the etching process is performed on an  
15 object to be processed 300. The object to be processed 300 is etched by using the silicon dioxide film layer 204 and the silicon nitride film layer 206 (hereinafter, referred to as 'mask material' together) as the mask material, thereby forming holes on the silicon layer 210, as illustrated in  
20 Fig. 3.

Hereinafter, plasma etching conditions in accordance with this embodiment will be described with reference to Table 1. Table 1 lists the etching conditions applied to a case where holes having a diameter of 0.15  $\mu\text{m}$  (design value)  
25 are formed in the silicon layer 210. Temperatures of the upper electrode 124, an inner wall of the processing chamber

102 and the lower electrode 104 are commonly set at 80 °C, 60 °C and 120 °C, respectively.

5 Table 1

Step	Pressure (mTorr)	Power (W)		Processing gas flow rate (sccm)					Pressure at backside of substrate (Torr)		Etch- ing time (sec)
		40.0	3.2	HBr	NF <sub>3</sub>	CF <sub>4</sub>	SiF <sub>4</sub>	O <sub>2</sub>	Central	Peripheral	
		HHz	MHz						portion	portion	
BT	50	400	100	150	2.5	0	0	1	13	15	10
S1	125	700	500	220	32	0	0	14	13	15	60
S2	200	600	500	270	35	0	0	3	10	15	20
S3	200	600	800	270	35	0	10	18	10	15	240
S4	200	600	800	270	35	10	10	18	10	15	240

The plasma etching method (plasma processing method) in accordance with this embodiment includes a plurality of steps, as shown in Table 1.

First of all, a breakthrough (BT) step is performed to remove a silicon dioxide film layer generated due to a natural oxidation on a surface of the silicon layer 210 to be etched (see Fig. 3).

Next, a first step S1 is performed to form holes having, e.g., a funnel shape, wherein a large inner diameter is provided at an upper portion and a small inner diameter

is provided at a lower portion. In order to form such shaped holes during the first step, the silicon layer 210 is etched such that the diameter of the holes becomes smaller as the etching progresses in the depth direction. At this time, the depth of the hole is, e.g., 1.5  $\mu\text{m}$ . The first step S1 can be divided into a number of steps and different etching conditions can be applied to each step. In such a case, it is possible to form holes having more conformal shapes to design values.

Thereafter, a second step S2, a third step S3 and a fourth step S4 are performed to further etch the silicon layer 210. After going through these steps, the holes formed in the silicon layer 210 can have a depth determined by the design value. As can be seen from Table 1, different etching conditions are applied to second, third and fourth steps S2, S3 and S4. By forming the holes while varying the etching conditions as described above, it is possible to obtain holes having a final shape corresponding to the design value.

As a result of performing the aforementioned steps, the holes each having a predetermined diameter and depth are formed in the object to be processed 300.

In case of forming fine holes in the silicon layer 210, the etching rate of silicon is deteriorated as the holes grow toward a lower portion of the silicon layer 210. Therefore, in the plasma etching method in accordance with

this embodiment, the output of the high frequency power supply 138 is increased during the latter steps of the etching process, i.e., the third and the fourth steps S3 and S4. Accordingly, the ion energy in the plasma increases such  
5 that the etching rate at a lower deep portion of the silicon layer 210 can be prevented from being deteriorated. Further, during the third and the fourth steps S3 and S4, the flow rate of O<sub>2</sub> gas is increased to accelerate an accumulation of a protective layer at a top portion of the mask material.  
10 As a result, a high etching selectivity can be obtained. Furthermore, it is preferable that the timing of increasing the output power of the high frequency power supply 138 be substantially equal to that of increasing the flow rate of O<sub>2</sub> gas.

15 Hereinafter, deposits accumulated at the openings of the mask material during the etching process of the silicon layer 210 will be described with reference to Figs. 4A to 4C.

In the plasma etching method in accordance with this embodiment, a gaseous mixture in which CF<sub>4</sub> gas is added to  
20 HBr gas, NF<sub>3</sub> gas (or SF<sub>6</sub> gas), SiF<sub>4</sub> gas and O<sub>2</sub> gas is used as the processing gas. Among them, HBr gas or SiF<sub>4</sub> gas in particular contributes to the forming of a protective layer on inner walls of the holes. Since the protective layer is formed on the inner walls of the holes, it is possible in  
25 this embodiment to vertically and highly precisely form fine holes having an opening diameter of 0.15 μm (design value)

in the silicon layer 210, as defined in the mask.

However, as the etching for forming holes in the silicon layer 210 progresses, deposits (e.g.,  $\text{SiBr}_x\text{O}_y$ , x and y being combination ratios) become excessively accumulated  
5 on the opening portions of the mask.

Fig. 4A shows a schematic cross sectional view of the object to be processed (a lower portion of the silicon layer 210 is omitted), when the third step S3 is completed, i.e., 330 seconds after the start of the etching process. Formed  
10 in the silicon layer 210 are holes 210a and 210b at this point not reaching a final depth thereof. Further, since the etching has been performed for 330 seconds, the silicon dioxide film layer 204 that used to have a thickness of D0 before the etching has a reduced thickness of Da (the  
15 remaining amount of silicon dioxide film layer mask), as measured with respect to shoulder portions at the entrance of the holes.

Additionally, as illustrated in Fig. 4A, deposits 310 are accumulated at the openings of the mask. Accordingly,  
20 the opening diameter Ra1 103 nm of the mask is narrower than the uppermost opening diameter Ra2 133 nm of the holes 210a and 210b.

Fig. 4B represents a schematic cross sectional view of the object to be processed (a lower portion of the silicon  
25 layer 210 is omitted) when the entire etching process has been completed by finishing the fourth step S4, i.e., 570



seconds after the start of the etching process. The etching process has been continuously performed on the silicon layer 210 for 240 seconds since the object to be processed reached the state illustrated in Fig. 4A and, accordingly, the thickness of the shoulder portion of the silicon dioxide film layer 204 formed at the entrance of the holes is reduced from  $D_a$  to  $D_b$ .

As shown in Fig. 4B, the deposits 310 are accumulated at the openings of the mask even after the entire etching process has been completed. However, the amount of the accumulated deposits 310 is small, and the opening diameter  $R_{b1}$  127 nm of the mask that is measured when the entire etching process has been completed is wider than the opening diameter  $R_{a1}$  103 nm of the mask that is measured when 330 seconds has passed since the start of the etching process.

Under the etching conditions in accordance with this embodiment, during the fourth step S4,  $CF_4$  gas is introduced into the processing chamber 102. Due to the  $CF_4$  gas, accumulation of deposits at the openings of the mask is suppressed. Hereinafter, effects of the  $CF_4$  gas will be described in detail.

Fig. 4C shows as in Fig. 4B, a schematic cross sectional view of the object to be processed obtained after the entire etching process has been completed by finishing the fourth step S4, i.e., 570 seconds after the start of the etching process. However, the object to be processed

illustrated in Fig. 4C is different from that shown in Fig. 4B in that the etching process of Fig. 4C is performed thereon by using a processing gas that does not contain  $\text{CF}_4$  gas. Specifically, during the etching process of the object to be processed shown in Fig. 4b,  $\text{CF}_4$  gas having a flow rate of 10 sccm was introduced into the processing chamber 102 in the fourth step S4 (see Table 1). On the other hand, while the object to be processed illustrated in Fig. 4C is etched,  $\text{CF}_4$  gas is not introduced into the processing chamber 102 during any steps of the etching process.

In other words, the difference between the etching conditions applied for obtaining the object to be processed illustrated in Fig. 4B and those for the object to be processed shown in Fig. 4C is whether or not the  $\text{CF}_4$  gas is introduced into the processing chamber 102. As clearly can be seen by comparing Figs. 4B to Fig. 4C, there is a big difference in the amount of accumulated deposits between the case where the  $\text{CF}_4$  gas is added to the processing gas and the case where the  $\text{CF}_4$  gas is not added thereto.

In case the  $\text{CF}_4$  gas is not added to the processing gas, the amount of the accumulated deposits 310 increases during a latter part of the etching process in which the holes are deeply formed. As a result, when the etching process is completed, the opening diameter Rcl of the mask becomes very narrow, i.e., 108 nm, as shown in Fig. 4C.

On the other hand, in case the  $\text{CF}_4$  gas is added to the

processing gas, the amount of the deposits 310 accumulated at the openings of the mask is small, as illustrated in Fig. 4B when the entire etching process is completed. Moreover, the opening diameter Rb1 127 nm of the mask is wider than the opening diameter Rc1 108 nm of the mask that is measured in case the processing gas does not contain the  $\text{CF}_4$  gas. This means that in case the  $\text{CF}_4$  gas is added to the processing gas, while the silicon layer 210 is being etched during the latter part of the etching process in which the holes are deeply formed, the opening diameter of the mask is large.

On the other hand, the uppermost opening diameter Rb2 140 nm of the holes 210a and 210b which is measured in case the  $\text{CF}_4$  gas is added to the processing gas, is not considerably different from the uppermost opening diameter Rc2 139 nm of the holes 210a and 210b which is measured in case the  $\text{CF}_4$  gas is not added to the processing gas. That is, even if the  $\text{CF}_4$  gas is added to the processing gas, the inner diameter of the holes formed in the silicon layer 210 is not enlarged to thereby form appropriately shaped holes.

However, the thicknesses Db and Dc of the silicon dioxide film layer 204 formed at the entrance of the holes become different between the two cases where the  $\text{CF}_4$  gas is added and not added to the processing gas. By comparing Fig. 4B with Fig. 4C, it can be seen that the etching rate of the silicon dioxide film layer 204 included in the mask material

increases in case the  $\text{CF}_4$  gas is added to the processing gas. Therefore, it is preferable to control the timing of introducing the  $\text{CF}_4$  gas into the processing chamber 102 and the flow rate thereof so that the silicon dioxide film layer 204 can remain at least until the etching process for forming holes on the silicon layer 210 is completed. The timing of introducing the  $\text{CF}_4$  gas into the processing chamber 102 and the flow rate thereof will be described later.

Hereinafter, the shapes of the holes formed on the silicon layer 210 by etching the silicon layer 210 under the etching conditions described in Table 1 will be described with reference to Figs. 5A to 5C.

Fig. 5A corresponding to Fig. 4A depicts the shapes of the holes 210a and 210b formed in the depth direction when 330 seconds has passed since the beginning of the etching process. Further, Fig. 5B corresponding to Fig. 4B describes the shapes of the holes 210a and 210b formed in the depth direction when the entire etching process has been completed by finishing the fourth step S4 where the  $\text{CF}_4$  gas is introduced into the processing chamber 102, i.e., when 570 seconds has passed since the beginning of the etching process. Furthermore, Fig. 5C corresponding to Fig. 4C indicates the shapes of the holes 210a and 210b formed in the depth direction when the entire etching process has been completed without introducing the  $\text{CF}_4$  gas into the

processing chamber 102, i.e., 570 seconds after the beginning of the etching process. Additionally, in order to show the accurate shapes of the holes, Figs. 5A to 5C represent the schematic cross sectional views of the objects to be processed that were cleaned by using a liquid chemical, e.g., hydrofluoric acid. Accordingly, protective layers formed on inner walls of the holes during the etching process or deposits accumulated at the openings of the mask material are not illustrated therein.

10       As shown in Fig. 5A, when 330 seconds has passed since the beginning of the etching process, the depth  $D_{sa}$  of the holes 210a and 210b reaches  $5.37\text{ }\mu\text{m}$ . Besides, at this point, the uppermost opening diameter  $R_{at}$  of the holes 210a and 210b is 162 nm, and the diameter  $R_{ab}$  of a bottom portion of  
15       the holes 210a and 210b is 127 nm.

      When the etching process (the fourth step S4) has been performed on the silicon layer 210 for 240 seconds after reaching the state shown in Fig. 5A obtained 330 seconds after the beginning of the etching process, the depth  $D_{sb}$  of  
20       the holes 210a and 210b reaches  $7.81\text{ }\mu\text{m}$ , as shown in Fig. 5B. During the fourth step S4, the  $\text{CF}_4$  gas is introduced into the processing chamber 102.

      In case the  $\text{CF}_4$  gas is not introduced thereinto during the fourth step S4, the depth  $D_{sc}$  of the holes 210a and 210b  
25       merely reaches  $7.65\text{ }\mu\text{m}$ , as illustrated in Fig. 5C.

      As clearly can be seen by comparing Fig. 5B with Fig.

5C, the depth of the holes formed in the silicon layer 210 becomes different between the cases where the  $\text{CF}_4$  gas is added or not added to the processing gas. Such difference originates from the difference in the amounts of the deposits 310 accumulated at the openings of the mask.

As illustrated in Fig. 4C, in case the  $\text{CF}_4$  gas is not added to the processing gas, the deposits 310 are excessively accumulated at the openings of the mask, thereby narrowing the opening diameter  $R_{c1}$  of the mask. As a result, an apparent aspect ratio of the holes 210a and 210b being formed increases. Herein, the "apparent aspect ratio" is defined as "a depth of the holes/the opening diameter  $R_{c1}$  of the mask".

If the apparent aspect ratio increases, the etching rate near a bottom portion of the holes 210a and 210b is remarkably deteriorated during the latter part of the etching process where the holes are deeply formed. Thus, it may be difficult to obtain a designed depth.

As shown in Fig. 4B, by adding the  $\text{CF}_4$  gas to the processing gas, accumulation of deposits 310 at the openings of the mask is suppressed, thereby enlarging the opening diameter  $R_{b1}$  of the mask. Accordingly, it is possible to avoid the deterioration of the etching rate near the bottom portion of the holes 210a and 210b during the latter part of the etching process where the holes are deeply formed, so that the desired depth of the holes can be obtained. In

case the  $\text{CF}_4$  gas is added to the processing gas during the fourth step S4, the etching rate of the silicon layer 210 during the fourth step S4 is 610 nm/min, which is a favorable value in comparison with the etching rate of the silicon layer 210, i.e., 570 nm/min, that is measured in case the  $\text{CF}_4$  gas is not added to the processing gas.

Further, in case the  $\text{CF}_4$  gas is added to the processing gas (Fig. 5B), the uppermost opening diameter  $R_{bt}$  of the holes 210a and 210b is 171 nm, and the diameter  $R_{bb}$  at the bottom of the holes 210a and 210b is 137 nm. On the other hand, in case the  $\text{CF}_4$  gas is not added to the processing gas (Fig. 5C), the uppermost opening diameter  $R_{ct}$  of the holes 210a and 210b is 168 nm, and the diameter  $R_{cb}$  at the bottom of the holes 210a and 210b is 135 nm. In other words, even if the  $\text{CF}_4$  gas is added to the processing gas, the inner diameter of the holes formed on the silicon layer 210 is not enlarged.

Hereinafter, the timing of introducing  $\text{CF}_4$  gas into the processing chamber 102 and the flow rate thereof will be described.

Table 2 indicates relationships between the flow rate of  $\text{CF}_4$  gas introduced into the processing chamber 102 and the etching rate and the in-surface uniformity (uniformity of the etching rate in surface of a semiconductor wafer) of the silicon dioxide layer 204 of the mask material.

Table 2

CF <sub>4</sub> gas flow rate (sccm)	Etching rate (nm/min)	In-surface uniformity (%)
0	55.5	± 8.2
5	70.4	± 15.9
10	79.3	± 15.9
30	117.6	± 9.6
50	153.8	± 16.7

If the flow rate of CF<sub>4</sub> gas introduced into the  
 5 processing chamber increases, the etching rate of the  
 silicon dioxide layer 204 also increases. Meanwhile, values  
 of the in-surface uniformity are nearly constant regardless  
 of variations in the flow rates of CF<sub>4</sub> gas. Therefore, it  
 is preferable to set the flow rate of CF<sub>4</sub> gas mainly  
 10 considering the etching rate. Specifically, the flow rate  
 thereof is controlled such that the silicon dioxide film  
 layer 204 in the mask material is not completely consumed  
 before the etching process for forming holes is completed.  
 For example, it is preferable to control the flow rate of  
 15 CF<sub>4</sub> gas within the range from about 5 to about 50 sccm.  
 Under the etching conditions in accordance with the  
 preferred embodiment, the flow rate of CF<sub>4</sub> gas is controlled  
 to be maintained at about 10 sccm, as illustrated in Table 1.

Hereinafter, the timing of introducing the CF<sub>4</sub> gas into



the processing chamber 102 and the period thereof in accordance with the preferred embodiment will be described with reference to Fig. 6. The period of introducing CF<sub>4</sub> gas into the processing chamber 102 (the period of adding CF<sub>4</sub> gas to the processing gas) can be set from the beginning to the end of the etching process, from the beginning to an intermediate stage of the etching process, or from a certain stage to the end of the etching process. Moreover, the CF<sub>4</sub> gas can be introduced into the processing container 102 during a predetermined time period in the etching process. The timing of introducing CF<sub>4</sub> gas into the processing container 102 and the period thereof are preferably determined based on the opening diameter or the depth of the holes 210a and 210b formed by the etching, the thickness of the silicon dioxide film layer 204 in the mask material, the types of the processing gas and the like.

The timing of introducing the CF<sub>4</sub> gas into the processing chamber 102 and the period thereof in the preferred embodiment will now be described. Fig. 6 shows a relationship between an etching time for forming the holes 210a and 210b in the silicon layer 210 and an opening diameter of the mask.

Referring to Fig. 6, there are illustrated a circle "O" indicating an opening diameter of the mask, which is measured when the CF<sub>4</sub> gas is not added to the processing gas; a square "□" representing an opening diameter of the

mask, which is measured when the  $\text{CF}_4$  gas is added to the processing gas from the beginning of the fourth step S4, i.e., 330 seconds after the beginning of the etching process; and a triangle " $\Delta$ " presenting an opening diameter of the mask, which is measured in case the  $\text{CF}_4$  gas is added to the processing gas from 90 seconds after the beginning of the etching process, i.e., in the middle of the third step S3. The introducing timing of  $\text{CF}_4$  gas represented by the square " $\square$ " in Fig. 6 corresponds to the etching conditions illustrated in Table 1.

According to the result represented by the circles "O" in Fig. 6, a large amount of deposits is accumulated at the openings of the mask during a period spanning from 90 to 330 seconds of the etching time. After 330 seconds has passed since the beginning of the etching process, the amount of newly accumulated deposits is small. During the period spanning from 90 to 330 seconds of the etching time, the depth of the holes 210a and 210b is shallow yet whereas the etching rate of the silicon layer 210 is high, so that a large amount of deposits is considered to be accumulated at the openings of the mask.

Therefore,  $\text{CF}_4$  gas can be added to the processing gas from 90 seconds after the beginning of the etching process (or from the beginning of the etching process) till 330 seconds after the beginning of the etching process (or to the end of the etching process), as plotted by the triangle

"Δ" instead of the square "□" representing the timing of introducing CF<sub>4</sub> gas corresponding to the etching conditions of Table 1. In this case, it is possible to suppress the accumulation of deposits itself at the openings of the mask.

5        Further, as plotted by the squares "□", the deposits accumulated at the openings of the mask are etched and removed by the CF<sub>4</sub> gas that is added to the processing gas since 330 seconds after the beginning of the etching process when the amount of newly accumulated deposits at the  
10       openings of the mask becomes negligible.

      By adding the CF<sub>4</sub> gas to the processing gas, the opening diameter of the mask is enlarged by about 20 nm in comparison with the case where the CF<sub>4</sub> gas is not added thereto. Moreover, by controlling the timing of adding the  
15       CF<sub>4</sub> gas to the processing gas, the effect of suppressing the accumulation of deposits at the openings of the mask and/or an effect of removing the deposits accumulated thereat can be achieved.

      The timing of adding the CF<sub>4</sub> gas to the processing gas  
20       is preferably set when the opening diameter of the mask becomes narrow (e.g., smaller than or equal to about 110 nm) so as to deteriorate the etching rate of the silicon layer 210 or when deposits are excessively accumulated at the openings of the mask. Furthermore, it is preferable to set  
25       the timing of stopping the addition of CF<sub>4</sub> gas to the processing gas to coincide with the time when the

accumulation of the deposits at the openings of the mask is stopped substantially (e.g., 330 seconds after the beginning of the etching process). Moreover, it is also possible to continuously add the  $\text{CF}_4$  gas until the end of the etching process. In this case, however, the flow rate of  $\text{CF}_4$  gas should be controlled at an appropriate value such that, especially, the silicon dioxide film layer 204 is not completely consumed.

As described above, in accordance with the plasma etching method of the preferred embodiment, an appropriate amount of  $\text{CF}_4$  gas is added to the processing gas having a mixture of  $\text{HBr}$  gas,  $\text{NF}_3$  gas (or  $\text{SF}_6$  gas),  $\text{SiF}_4$  gas and  $\text{O}_2$  gas at an appropriate timing. Due to an effect of the  $\text{CF}_4$  gas, the accumulation of deposits at the openings of the mask is suppressed and, further, accumulated deposits can be removed. Accordingly, it is possible to form deep holes in the silicon layer 210 even in case the diameter of the openings of the mask is very small.

Although the present invention has been described with respect to the preferred embodiments where holes are formed in a silicon layer by the etching, the present invention can be applied to a case where grooves are formed in a silicon layer. Similar effects can be obtained when forming either grooves or holes in a wafer, e.g., a silicon layer. Further, in case the grooves are formed in the wafer, an opening diameter of the aforementioned holes corresponds

to an opening width of the grooves.

The preferred embodiments of the present invention have been described where the  $\text{CF}_4$  gas is added to the processing gas. However, in lieu of the  $\text{CF}_4$  gas, a CF-based  
5 gas such as  $\text{C}_4\text{F}_8$  gas,  $\text{C}_5\text{F}_8$  gas and  $\text{C}_4\text{F}_6$  gas and the like or CHF-based gas such as  $\text{CHF}_3$  gas,  $\text{CH}_2\text{F}_2$  gas and the like can be added to the processing gas. Similar effects of preventing deposits from being accumulated at the openings of the mask material can be obtained by employing any of the  
10 aforementioned gases.

In addition, although the plasma etching method in accordance with the preferred embodiments of the invention uses a processing gas containing either the  $\text{SF}_6$  gas or the  $\text{NF}_3$  gas, the present invention is not limited thereto. Even  
15 if a processing gas containing both the  $\text{SF}_6$  gas and the  $\text{NF}_3$  gas is used, similar effects can be obtained.

While the invention has been shown and described with respect to the preferred embodiments, it will be understood by those skilled in the art that various changes and  
20 modification may be made without departing from the spirit and scope of the invention as defined in the following claims.